

METHOD FOR MANUFACTURING TERBIUM ALUMINUM-BASED
PARAMAGNETIC GARNET SINGLE CRYSTAL

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates to a method for manufacturing a terbium aluminum-based paramagnetic garnet single crystal containing at least Tb and Al. For example, the present invention relates to a method for manufacturing a terbium aluminum-based paramagnetic garnet single crystal used for optical isolators, optical circulators, and the like for optical communication and optical recording.

10 2. Description of the Related Art

 In recent years, the speeds and capacities of communication devices including conventional metal communication lines have become insufficient due to an increase in the amount of information communication, and therefore, an optical communication technology has been noted as a high-speed, large-capacity information communication technology. Research and development on the high-speed, large-capacity information communication technology employing the use of extremely low-loss transmission characteristic of a quartz fiber in the infrared region (wavelength is 1,300 to 1,600 nm) in combination with high-density wavelength division multiplexing technology (DWDM) have been actively pursued as the currently predominant optical communication technology.

 An improvement in the characteristics of and reduction in the cost of optical components supporting the optical communication technology in terms of hardware become important. Under these circumstances, magneto-optical devices based on the interaction between light and magnetism has also become important. The magneto-optical devices are required to have material characteristics including, in particular, (1) a large Faraday effect and (2) a high light-transmittance.

Magnetic materials satisfying the above-described conditions include a single crystal of terbium aluminum paramagnetic garnet ($\text{Tb}_3\text{Al}_5\text{O}_{12}$; hereafter referred to as TAG) containing Tb and Al. This TAG single crystal has a Verdet constant ($\text{deg}/(\text{Oe}\cdot\text{cm})$) significantly larger than that of the other paramagnetic materials, where
5 the Verdet constant shows the magnitude of a Faraday rotation angle of a paramagnetic material on a unit length and a unit magnetic field basis. Consequently, a sufficient Faraday rotation angle can be achieved even when the size of the single crystal is decreased, and thereby, the magneto-optical device can be miniaturized. Since the magnet for applying a magnetic field can be made small, not only the
10 magneto-optical device itself can be miniaturized, but also the influence of the magnetic field on the other electronic components can be reduced to a minimum level, and the functions of the magneto-optical device can be stabilized. Furthermore, the TAG single crystal has sufficiently high light-transmittance in a wide wavelength range of light of 500 nm to 1,400 nm. In particular, it is also clear that a high light-
15 transmittance can be achieved in the visible light range in which the wavelength of light is 400 nm to 700 nm. It is desired to make full use of the TAG single crystal having such excellent characteristics for magneto-optical devices.

However, the TAG single crystal having such excellent characteristics is an incongruent melting type compound, and there is a problem in that melt composition
20 resulting from melting of the starting material is different from the crystal composition resulting from cooling of the melt. Specifically, the micro pull-down method (μ -PD method) shown in V.I. Chani et al., *J. Crystal Growth* 212 (2000) 469-475, the Czocklarski (Cz) method shown in S. Ganschow et al., *Cryst. Res. Technol.*, 34 (1999) 615 and the like are conventionally used. More specifically, in the micro pull-down
25 method, an opening is provided at the bottom of a crucible made of Pt, and a seed crystal is arranged at the opening of the crucible from the outside of the crucible. A polycrystal separately put into the crucible is heat-melted, and the seed crystal and the polycrystal are joined. The seed crystal is pulled down from the outside, and thereby, a single crystal grows. In the Czocklarski method, a calcined mixed powder of Tb_4O_7
30 and Al_2O_3 as starting materials is filled in an Ir crucible, and is melted by high-

frequency induction heating. After the seed crystal is brought into contact with the molten liquid so as to sufficiently conform the molten liquid, the seed crystal is pulled up while being rotated at a constant speed, and thereby, a TAG single crystal grows. However, when such a direct melt-textured growth process is used, with respect to the
5 incongruent melting type TAG single crystal, the garnet phase TAG single crystal cannot be directly produced from a melt composition of molten starting materials, and there is a problem in that perovskite phase TbAlO_3 is also present in addition to the TAG single crystal. In consideration of the above-described problem, it is attempted to form through the use of a flux method shown in C. B. Rubinstein et al., J. Appl.
10 Phys., 35 (1964) 3069. Specifically, a solution is prepared in the flux method, in which Tb_4O_7 and Al_2O_3 as starting materials are dissolved as solutes into a solvent of PbF_2 or the like. The seed crystal is put into this solution, followed by gradual cooling, and thereby, a bulk type TAG single crystal is produced. However, when these manufacturing methods are used, a few days to a few weeks are required for
15 production of the TAG single crystal, and furthermore, only a small crystal having a length of a short 1 to 2 mm can be produced. Therefore, no TAG single crystal having a practicable size can be produced.

For the above-described reasons, no TAG single crystal can be produced, or
20 only a small crystal can be produced. Consequently, no TAG single crystal having excellent characteristics can become in practical use as a material for an magneto-optical device.

SUMMARY OF THE INVENTION

The present invention overcomes the above-described problems. Accordingly,
25 it is an object of the present invention to provide a method for manufacturing a terbium aluminum-based paramagnetic garnet single crystal, which can easily produce a TAG single crystal having a large Faraday effect and a high light-transmittance even in the visual light range, and therefore, usable as a material for a magneto-optical device.

In order to achieve the above-described objects, a method for manufacturing a terbium aluminum-based paramagnetic garnet single crystal according to a first aspect of the present invention is a method for manufacturing a terbium aluminum-based paramagnetic garnet single crystal grown by a laser FZ method using a raw material rod made of paramagnetic garnet containing at least Tb and Al and a seed crystal, while at least one of the above-described raw material rod and the above-described seed crystal is porous, and the method includes the steps of preparing the above-described raw material rod, as a first step, preparing the above-described seed crystal, and melt-joining the above-described raw material rod and the above-described seed crystal, as a second step, heat-melting the joint of the above-described seed crystal and the above-described raw material rod by application of optical energy thereto so as to prepare a melt zone, as a third step, and cooling the resulting melt zone, as a fourth step.

By adopting the above-described manufacturing method, a TAG single crystal can easily be generated while generated TbAlO_3 is removed from the melt zone, and the TAG single crystal having a size which cannot be achieved by conventional manufacturing methods can easily be produced. In this manner, the number of chips cut from the TAG single crystal can be increased, and therefore, full use as a material for magneto-optical devices can be made. With respect to incongruent melting type $\text{Tb}_3\text{Al}_5\text{O}_{12}$ in the conventional manufacturing method, TbAlO_3 is initially generated in the solid-liquid interface between the melt zone and the solid, and thereafter, $\text{Tb}_3\text{Al}_5\text{O}_{12}$ is generated. Consequently, TbAlO_3 and $\text{Tb}_3\text{Al}_5\text{O}_{12}$ are inevitably brought into a mixed state. However, the inventors of the present invention found that when the joint of a seed crystal and a raw material rod was heat-melted, the molten liquid penetrates into a porous medium, and an initial phase of TbAlO_3 was deposited on a priority basis in the porous medium. Consequently, at least one of the seed crystal and the raw material rod is adjusted to be porous, the joint, that is, the solid-liquid interface between the melt zone and the solid, is heat-melted by application of optical energy thereto, and therefore, the initial phase of TbAlO_3 is deposited in this porous

medium, so that TbAlO_3 is removed from the melt zone, and thereby, a larger $\text{Tb}_3\text{Al}_5\text{O}_{12}$ single phase can be achieved.

With respect to a method for manufacturing a terbium aluminum-based paramagnetic garnet single crystal according to a second aspect of the present invention, preferably, one of the above-described raw material rod and the above-described seed crystal has a density of about 55% or more, but 100% or less, and the other has a density of about 55% or more, but about 85% or less.

By adjusting the raw material rod and the seed crystal to have the densities within the above-described range, TbAlO_3 is prevented from depositing in the single crystal, and the $\text{Tb}_3\text{Al}_5\text{O}_{12}$ single crystal can be stably formed. The term “density” here represents the relative density with respect to the theoretical density of the starting material composition.

With respect to a method for manufacturing a terbium aluminum-based paramagnetic garnet single crystal according to a third aspect of the present invention, preferably, the above-described seed crystal has a density of about 55% or more, but about 85% or less and the above-described raw material rod has a density of about 55% or more, but 100% or less.

By adjusting the raw material rod and the seed crystal to have the densities within the above-described range, TbAlO_3 is prevented from depositing in the single crystal, and the $\text{Tb}_3\text{Al}_5\text{O}_{12}$ single crystal can be stably formed. Furthermore, a larger $\text{Tb}_3\text{Al}_5\text{O}_{12}$ single crystal having a diameter of about 3 mm or more can be stably formed.

With respect to a method for manufacturing a terbium aluminum-based paramagnetic garnet single crystal according to a fourth aspect of the present invention, preferably, one of a $\text{Tb}_3\text{Al}_5\text{O}_{12}$ single crystal, a $\text{Tb}_3\text{Al}_5\text{O}_{12}$ polycrystal and $\text{Y}_3\text{Al}_5\text{O}_{12}$ is used as the above-described seed crystal.

When the seed crystal according to the fourth aspect of the present invention is used in the first to third aspects of the present invention, the seed crystal is likely to be melt-joined to the raw material rod containing at least Tb and Al. This provides advantages in that the TAG-based single crystal can be produced while TbAlO_3 is

prevented from depositing in the single crystal, and the TAG-based single crystal has a size which cannot be conventionally achieved.

With respect to a method for manufacturing a terbium aluminum-based paramagnetic garnet single crystal according to a fifth aspect of the present invention, preferably, $\text{Tb}_3\text{Al}_5\text{O}_{12}$ or $(\text{RTb})_3\text{Al}_5\text{O}_{12}$ (where R represents at least one of the rare-earth elements) is used as the above-described raw material rod. It is advantageous to use the fifth aspect in the first to third aspects because even when a rare-earth element, e.g. Dy, Ho, Er or Tm, is substituted for Tb in the basic composition of the terbium aluminum-based paramagnetic garnet single crystal, as described above, the TAG-based single crystal can be produced while TbAlO_3 is prevented from depositing in the single crystal, and the TAG-based single crystal has a large size and excellent quality which cannot be conventionally achieved.

With respect to a method for manufacturing a terbium aluminum-based paramagnetic garnet single crystal according to a sixth aspect of the present invention, preferably, the joint of the above-described raw material rod and the above-described seed crystal is heat-melted by application of CO_2 gas laser light thereto in the above-described third step.

By adopting the above-described manufacturing method, the raw material rod can efficiently absorb the laser light, and the joint of the seed crystal and the raw material rod can easily be heat-melted.

With respect to a method for manufacturing a terbium aluminum-based paramagnetic garnet single crystal according to a seventh aspect of the present invention, preferably, the laser light is condensed before the laser light is applied to the joint of the above-described raw material rod and the above-described seed crystal, in the above-described third step.

By adopting the above-described manufacturing method, the laser light is intensively applied to a part of the joint of the seed crystal and the raw material rod, and thereby, steeper, larger optical energy can be applied.

As described above, by adopting the method for manufacturing a terbium aluminum-based paramagnetic garnet single crystal according to the present invention,

the TAG single crystal can easily be produced, and the TAG-based single crystals can be suitably used as materials for magneto-optical devices.

By adopting the method for manufacturing a terbium aluminum-based paramagnetic garnet single crystal according to the second aspect of the present invention, the raw material rod and the seed crystal are adjusted to have the densities within the above-described range. Consequently, TbAlO_3 is prevented from depositing in the single crystal, and the $\text{Tb}_3\text{Al}_5\text{O}_{12}$ single crystal can be stably formed.

By adopting the method for manufacturing a terbium aluminum-based paramagnetic garnet single crystal according to the third aspect of the present invention, the raw material rod and the seed crystal are adjusted to have the densities within the above-described range. Consequently, TbAlO_3 is prevented from depositing in the single crystal, and the $\text{Tb}_3\text{Al}_5\text{O}_{12}$ single crystal can be stably formed. Furthermore, a larger $\text{Tb}_3\text{Al}_5\text{O}_{12}$ single crystal having a diameter of about 3 mm or more can be stably formed.

By using the seed crystal according to the fourth aspect of the present invention, the seed crystal is likely to be melt-joined to the paramagnetic garnet polycrystal containing at least Tb and Al. This provides advantages in that the TAG-based single crystal can be produced while TbAlO_3 is prevented from depositing in the single crystal, and the TAG-based single crystal has a size which cannot be conventionally achieved.

With respect to the method for manufacturing a terbium aluminum-based paramagnetic garnet single crystal according to the fifth aspect of the present invention, even when a rare-earth element, e.g. Dy, Ho, Er or Tm, is substituted for Tb, a large TAG-based single crystal having excellent quality can be produced, and therefore, the method serves a useful function.

By adopting the method for manufacturing a terbium aluminum-based paramagnetic garnet single crystal according to the sixth aspect of the present invention, the melt zone in the joint of the raw material rod and the seed crystal can efficiently absorb the laser light, and the melting can be performed with ease. In this

manner, large optical energy can be applied to the solid-liquid interface between the melt zone and the solid in the joint of the seed crystal and the raw material rod.

By adopting the method for manufacturing a terbium aluminum-based paramagnetic garnet single crystal according to the seventh aspect of the present invention, the laser light is intensively applied to a part of the joint of the seed crystal and the raw material rod, and thereby, large optical energy can be applied.

BRIEF DESCRIPTION OF THE DRAW MATERIALINGS

Fig. 1 is a schematic perspective view of a laser FZ apparatus according to an embodiment of the present invention;

Fig. 2 is a vertical, sectional photograph in the vicinity of a joint of $\text{Tb}_3\text{Al}_5\text{O}_{12}$ and a seed crystal according to the present invention;

Fig. 3 is a graph showing a positional dependence of the Al composition relative to the Tb composition in a $\text{Tb}_3\text{Al}_5\text{O}_{12}$ single crystal prepared by the manufacturing method of the present invention;

Figs. 4A and 4B are reflection X-ray Laue photographs of a $\text{Tb}_3\text{Al}_5\text{O}_{12}$ single crystal according to the present invention and a seed crystal, respectively;

Figs. 5A and 5B are graphs showing the measurement results of the material identification of a $\text{Tb}_3\text{Al}_5\text{O}_{12}$ single crystal according to the present invention and a reference crystal, respectively, with an X-ray diffractometer; and

Fig. 6 is a graph showing a Pole-Figure of the $\langle 111 \rangle$ orientation of a $\text{Tb}_3\text{Al}_5\text{O}_{12}$ single crystal according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preferred embodiments of the present invention will be described below.

In the present invention, at least one of the raw material rod and the seed crystal is porous. By using such raw material rod and/or seed crystal, an initial phase of TbAlO_3 is deposited on a priority basis in the porous medium, so that TbAlO_3 is removed from the melt zone, and thereby, a $\text{Tb}_3\text{Al}_5\text{O}_{12}$ single phase can be produced.

Preferably, one of the above-described raw material rod and the above-described seed crystal has a density of about 55% or more, but 100% or less, and the other has a density of about 55% or more, but about 85% or less.

5 More preferably, the above-described seed crystal has a density of about 55% or more, but about 85% or less and the above-described raw material rod has a density of about 55% or more, but 100% or less. When the densities are adjusted to be within the above-described range, a larger $\text{Tb}_3\text{Al}_5\text{O}_{12}$ single crystal having a diameter of about 3 mm or more can be stably formed.

10 If the density of the raw material rod or the seed crystal is smaller than about 55%, the molten liquid excessively penetrates therein. Consequently, if the density of the raw material rod is smaller than about 55%, the melt zone becomes significantly slender, and problems occur in that only a slender single crystal is produced or the joint is broken. In particular, when the density of the seed crystal is less than about 55%, the strength is also reduced, and there is a problem in that the single crystal
15 cannot be sufficiently held. If the density of the seed crystal is more than about 85%, the molten liquid cannot sufficiently penetrate into the porous medium and TbAlO_3 cannot be sufficiently removed from the melt zone, and may deposit in the single crystal.

20 Since $\text{Tb}_3\text{Al}_5\text{O}_{12}$ is an incongruent melting type compound, an initial phase of TbAlO_3 and a liquid phase result by incongruent melting when the crystal is melted. When the seed crystal and the raw material rod are joined, followed by heat-melting, the molten liquid penetrates into the holes in the seed crystal and the raw material rod. It is clear that TbAlO_3 is deposited on a priority basis in the porous medium at this time, and TbAlO_3 locates at the boundary between the melt zone and the raw material
25 rod. On the other hand, the single crystal grows on the seed crystal. Since the density of the single crystal is 100%, the molten liquid penetrates simply in the raw material rod side during growth of the crystal. When the raw material rod and the seed crystal are moved in the same direction during growth of the crystal, TbAlO_3 also moves together with the melt zone in order to always locate at the boundary between the melt
30 zone and the raw material rod. When the density of the raw material rod is about 55%

or more, but 100% or less at this time, excessive penetration of the molten liquid can be prevented. However, if the density is smaller than about 55%, the molten liquid excessively penetrates into the raw material rod. Consequently, the melt zone cannot be stably held, and thereby, the melt zone is broken.

5 Preferably, the density of the seed crystal is smaller than that of the raw material rod. That is, the molten liquid is made to penetrate into the seed crystal side immediately after the heat-melting of the joint and the initial phase of TbAlO_3 is made to deposit, and thereby, TbAlO_3 can be reliably prevented from depositing in the single crystal.

10 Even when the density of the seed crystal is more than about 85%, but 100% or less, and the density of the raw material rod is about 55% or more, but about 85% or less, a TAG single crystal having a diameter in the order of 1 mm can be stably supplied as a matter of course.

15 Examples of methods for manufacturing the above-described porous raw material rod and seed crystal can include, for example, a method in which starting materials, an organic binder and a solvent are mixed so as to prepare a mixture in a slurry state, and thereafter, the resulting mixture is sintered. Here, the TAG polycrystal is sintered at a firing temperature of about 1,500°C to 1,600°C. A low density TAG polycrystal is prepared by sintering at a lower temperature. The range of
20 density of the TAG polycrystal of the present invention is adjusted by firing at a firing temperature of about 1,400°C to 1,600°C. In addition to this, the manufacture can be performed by changing the amount of addition of the above-described organic binder or by adjusting the firing time. The raw material rod used here is molded into the shape of a cylindrical column. However, any shape can be adopted as long as the
25 shape is convenient for melt-joining to the seed crystal described below. For example, the shape of a rod, a thin plate and the like can also be adopted.

30 Explanations will be made with reference to a single crystal manufacturing apparatus suited for manufacturing the terbium aluminum-based paramagnetic garnet single crystal of the present invention. Fig. 1 is a schematic perspective view of a laser FZ (Floating zone) apparatus according to an embodiment of the present

invention. This laser FZ apparatus 1 is composed of laser apparatuses 5 for lasing, a box 3 doubling as a radiating plate, in which an atmosphere can be adjusted, and a shaft 2 vertically movable in the box 3. The shaft 2 is a rod-shaped support which can be separated into an upper shaft 2a and a lower shaft 2b. The vertically movable shaft 2 is provided penetrating from the top surface to the bottom surface of the box 3. Each of the upper shaft 2a and the lower shaft 2b can hold a target. Window portions 4 are provided on both side surfaces of the box 3, and window portion lenses 4a are fit into the windows 4 in order that the laser light can be intensively applied to the joint of the target supported by the shaft 2a and the target for supporting supported by the shaft 2b. The laser apparatuses 5 are provided on both the side portions of the box 3 in order that the laser light can be applied through both window portions 4 of the box 3. The laser lights are emitted from the laser apparatuses 5 located in both side portions of the box 3, and thereby, the laser light is intensively applied from both directions to the targets supported by the shaft 2 through the window portion lenses 4a fit into the window portions 4 of the box 3.

The configuration in which shaft 2 can be moved in the axis direction, as described above, is preferable because the melting due to heating and solidification due to cooling can be successively performed. Preferably, the movement speed of the shaft is about 30 mm/hour or less, depending on the diameter of the TAG polycrystal used as the material. If the movement speed of the melt zone in the axis direction exceeds about 30 mm/hour, the crystal cannot be sufficiently melted, and it is difficult to convert the melt zone into a single crystal.

As the laser apparatus 5 used here, a CO₂ gas laser is preferable. Since the CO₂ gas laser apparatus emits a laser light having a long wavelength and a TAG polycrystal having a wide transparent wavelength range can efficiently absorb the laser light, and therefore, the TAG polycrystal is melt-joined with ease. Alternatively, an excimer laser or the like may be used.

Two laser apparatuses 5 are provided here on both the side portions of the box 3, and the laser lights are applied to the shaft 2 from both side surfaces. However, the locations of arrangement of the laser apparatuses 5 are not limited to these. That is, it

is essential only that the optical energy of the laser light is intensively applied to the joint of the TAG polycrystal and the seed crystal, and at least three laser apparatuses may be provided so that the laser light may also be applied from the location on the normal to the above-described joint. When a plurality of lasing sources are prepared,
5 as described above, a steeper temperature gradient can be applied, and in addition, the irradiation area can be increased as well. Consequently, a TAG single crystal having a larger size can be produced.

The intensity of the laser light can be adjusted by adjusting the distance from the laser apparatus 5 to the shaft 2 holding a paramagnetic garnet single crystal 7 and a
10 seed crystal 8. These laser lights can appropriately be adjusted depending on the size of the resulting crystal, the size of the box 3, the focal length of the lens 4 and the like.

In the present invention, a condenser lens element 6 is preferably, separately provided in order to apply the laser light more intensively to the end portion of the TAG polycrystal. Specifically, the condenser lens element 6 having a condenser lens
15 6a is an extension of the window portion of the box 3 and a lasing hole 5a of the laser apparatus 5, and is provided in such a location that the laser light is concentrated onto the end portion of the target for supported with the upper shaft 2a, through the window portion 4 of the box 3. The condenser lens 6a is not necessarily the same lens as the window portion lens 4a of the window portion 4 of the box 3. When a CO₂ gas laser
20 is used, preferably, the condenser lens 6a is made of ZnSe. Other condenser lenses can also be used as long as those are devices capable of condensing the laser light.

The targets are the raw material rod and the seed crystal. The raw material rod may be held on the shaft 2a and the seed crystal may be held on the shaft 2b, or the seed crystal may be held on the shaft 2a and the raw material rod may be held on the
25 shaft 2b.

The shaft 2a and the shaft 2b may be rotated at the same speed in the same direction in order that the laser light can be applied to a wide range of the joint of the target for supporting held on the shaft 2a and the target for supporting held on the shaft 2b.

The TAG-based single crystals prepared by the method for manufacturing a terbium aluminum-based paramagnetic garnet single crystal of the present invention can be used for magneto-optical devices, specifically, optical isolators, optical attenuators, optical switches, optical circulators and the like. Furthermore, the TAG-based single crystals can be used as materials for various magneto-optical sensors, e.g. rotation sensors, flow rate sensors and current sensors.

Experimental example 1

A preferred embodiment of the method for manufacturing a terbium aluminum-based paramagnetic garnet single crystal of the present invention will be more specifically described below.

Example 1

1. First step

As starting materials for a raw material rod, Tb_4O_7 (purity 99.9%) and Al_2O_3 (purity 99.99%) were prepared, followed by weighing in order to constitute $\text{Tb}_3\text{Al}_5\text{O}_{12}$. Pure water was added to the resulting mixed powder of the starting materials, and mixing was done for about 24 hours together with cobbles. The resulting mixed powder was dehydrated with an aspirator, and dried with a drier. The resulting mixed powder was passed through a mesh so as to adjust the particle size of the mixed powder, and then calcined in an electric furnace at $1,200^\circ\text{C}$ for 2 hours. After this calcining, the resulting mixed powder was pulverized, and an organic binder and a solvent were added thereto, and then mixed for a few hours together with cobbles, so that a mixture in a slurry state was prepared. The resulting mixture was molded into the shape of a cylindrical column with a molding apparatus, followed by firing again in an electric furnace at $1,600^\circ\text{C}$ for 2 hours, so that a cylindrical TAG polycrystal was produced. The resulting TAG polycrystal had a density of 80%.

2. Second step

The TAG polycrystal prepared in the first step is molded into the shape of a cylindrical column having a diameter of 1 mm. The laser FZ apparatus 1 shown in

Fig. 1 is used. The resulting cylindrical TAG polycrystal 7 is arranged while being held on one end of the upper shaft 2a of the laser FZ apparatus, and a seed crystal 8 made of a TAG single crystal is arranged at one end of the lower shaft 2b. The atmosphere in the box 3 is air, and the laser lights are applied from the laser apparatuses 5. Consequently, the end portion of the TAG polycrystal 7 arranged at one end of the upper shaft 2a is heated to the order of 1,900°C so as to be melted, and the molten portion is joined to the end portion of the seed crystal 8 arranged on the lower shaft 2b. The distance from the laser apparatus 5 to the shaft 2 holding the paramagnetic garnet single crystal 7 and the seed crystal 8 is adjusted to be about 50 cm. As the laser apparatus 5 used here, specifically, a CO₂ gas laser apparatus capable of emitting a CO₂ gas laser light having a wavelength of 10.6 μm is used, and the output thereof is adjusted at 60 W.

3. Third step

A melt zone is formed by joining the end portion of the TAG polycrystal 7 and the end portion of the seed crystal 8 while the laser lights are applied thereto.

4. Fourth step

The shaft is moved in the axis direction at a speed of 30 mm/hour or less, and thereby, the melt zone is moved from the location irradiated with the laser light. In this manner, the melt zone is cooled, so that a crystal is produced.

Evaluation was performed by the following methods with respect to whether the crystal produced as described above was a desired TAG single crystal. (1) Vertical, sectional photographs were taken with respect to the vicinity of the joint of the Tb₃Al₅O₁₂ single crystal used as the seed crystal and the resulting crystal. Fig. 2 reproduces a photograph of the seed crystal indicated as region 1 and the resulting crystal indicated as region 2. (2) With respect to the region 1 and the region 2, the surface of each crystal was irradiated with an electron beam, and thereby, a positional dependence of the Al composition relative to the Tb composition was measured by line analysis using the WDX method (Wavelength Dispersive X-ray Spectroscopy) in which a characteristic X-ray inherent in the element contained in the crystal was detected. This is shown in Fig. 3. (3) A reflection X-ray Laue photograph was taken

with respect to each of the $\text{Tb}_3\text{Al}_5\text{O}_{12}$ single crystal used as the seed crystal and the resulting crystal. This is shown in Fig. 4A. (4) The material identification was performed with an X-ray diffractometer which measured diffraction peaks based on the irradiation of the resulting crystal with an X-ray. The results are shown in Fig. 5.

5 As is clear from Fig. 2, no phase other than the garnet phase is deposited in the vicinity of the joint of region 1 (indicating the seed crystal) and region 2 (indicating the resulting crystal). With respect to the positional dependence of the Al composition relative to the Tb composition, Al/Tb is a constant 1.67 at every position in the resulting crystal, as is clear from Fig. 3. In this manner, it is clear that the
10 compositional ratio of Al to Tb is the same at every position in region 1 and region 2. Furthermore, since the reflection X-ray Laue image of the $\text{Tb}_3\text{Al}_5\text{O}_{12}$ single crystal used as the seed crystal shown in Fig. 4A is in agreement with that of the resulting crystal shown in Fig. 4B, it is clear that the growing orientation can be controlled as well. Fig. 5B is a JCPDS card showing X-ray peak values of the garnet phase. X-ray
15 peak values of the resulting crystal shown in Fig. 5A are in agreement with the X-ray peak values of the garnet phase shown in Fig. 5B, and no X-ray peak value other than that of the garnet phase was detected. In this manner, it is clear that the resulting crystal is a single phase of TAG. As is clear from the above-described results, the resulting crystal is a TAG single crystal represented by $\text{Tb}_3\text{Al}_5\text{O}_{12}$.

20 As is clear from the measurement of the shape of the resulting TAG single crystal, a fiber-shaped TAG single crystal of 1 mm in diameter and 27 mm in length is produced.

Example 2

As starting materials for a raw material rod, Tb_4O_7 (purity 99.9%) and Al_2O_3
25 (purity 99.99%) were weighed, and a TAG polycrystal was prepared in a manner similar to that in Example 1. The density of the resulting TAG polycrystal was 80%. In the second step, a crystal was prepared in a manner similar to that in Example 1 except that the resulting TAG polycrystal 7 was held on one end of the upper shaft 2a of the laser FZ apparatus 1, and furthermore, this resulting TAG polycrystal 7 was

arranged at one end of the lower shaft 2b as a seed crystal. Evaluation was performed by the following method with respect to whether the thus prepared crystal was a TAG single crystal. The resulting fiber-shaped crystal was cut in the direction of the radius to have the shape of a chip. This was set in an HR-XRD apparatus (X' pert

5 manufactured by Philips), the diffraction angle was fixed in order that the reflection of the 100 appeared in the $\langle 111 \rangle$ orientation of the TAG single crystal, and the Pole-Figure was measured. The results thereof are shown in Fig. 6.

In Fig. 6, an arrow indicates the ϕ coordinate, the center of the concentric circles is $\phi = 0$, and the outermost circle indicates $\phi = 90^\circ$. With respect to the
10 resulting crystal, four reflections of the 100 forming an angle of $\phi = 69^\circ$ with each other were identified and no other reflection of the 100 appeared.

Laue photographs were taken in a manner similar to that in (3) of Example 1. The reflection X-ray Laue image of the $\text{Tb}_3\text{Al}_5\text{O}_{12}$ single crystal is in agreement with that of the resulting crystal, and therefore, it is clear that the growing orientation can
15 be controlled as well. The material identification of the resulting crystal was performed with an X-ray diffractometer in a manner similar to that in (4) of Example 1, and no X-ray peak value other than that of the garnet phase was detected. It is clear from the above description that the resulting crystal is a single phase of $\text{Tb}_3\text{Al}_5\text{O}_{12}$. In this manner, it is clear that the resulting crystal is a TAG single crystal.

20 Example 3

As starting materials for a raw material rod, Tb_4O_7 (purity 99.9%) and Al_2O_3 (purity 99.99%) were weighed, and a TAG polycrystal was prepared in a manner similar to that in Example 1. The density of the resulting TAG polycrystal was 80%. A crystal was prepared in a manner similar to that in Example 1, except that a
25 $\text{Y}_3\text{Al}_5\text{O}_{12}$ single crystal was used as the seed crystal. With respect to the thus prepared crystal and the TAG single crystal, Laue photographs were taken in a manner similar to that in (3) of Example 1 and comparisons were performed. The reflection X-ray Laue image of the resulting crystal is in agreement with that of the TAG single crystal, and therefore, it is clear that the growing orientation can be controlled as well. The

material identification of the resulting crystal was performed with an X-ray diffractometer in a manner similar to that in (4) of Example 1, and no peak other than that of the garnet phase was detected. It is clear from the above description that the resulting crystal is a TAG single crystal.

5 Example 4

As starting materials for a raw material rod, Tb_4O_7 (purity 99.9%), Al_2O_3 (purity 99.99%) and Dy_2O_3 (purity 99.9%) were weighed in order to constitute $DyTb_2Al_5O_{12}$, and a $DyTb_2Al_5O_{12}$ polycrystal was prepared in a manner similar to that in Example 1. The density of the resulting $DyTb_2Al_5O_{12}$ polycrystal was 80%. A
10 crystal was prepared in a manner similar to that in Example 1 except that a $DyTb_2Al_5O_{12}$ single crystal was used as the seed crystal. With respect to the thus prepared crystal, Laue photographs were taken in a manner similar to that in (3) of Example 1. The reflection X-ray Laue image of the $DyTb_2Al_5O_{12}$ single crystal used as the seed crystal is in agreement with that of the resulting crystal, and therefore, it is
15 clear that the growing orientation can be controlled as well. The material identification of the resulting crystal was performed with an X-ray diffractometer in a manner similar to that in (4) of Example 1, and no X-ray peak value other than that of the garnet phase was detected. It is clear from the above description that the resulting crystal is a single phase of $DyTb_2Al_5O_{12}$ single crystal.

20 Example 5

As starting materials for a raw material rod, Tb_4O_7 (purity 99.9%), Al_2O_3 (purity 99.99%) and Ho_2O_3 (purity 99.9%) were weighed in order to constitute $Ho_{0.5}Tb_{2.5}Al_5O_{12}$, and a $Ho_{0.5}Tb_{2.5}Al_5O_{12}$ polycrystal was prepared in a manner similar to that in Example 1. The density of the resulting $Ho_{0.5}Tb_{2.5}Al_5O_{12}$ polycrystal was
25 80%. A crystal was prepared in a manner similar to that in Example 1 except that a $Ho_{0.5}Tb_{2.5}Al_5O_{12}$ single crystal was used as the seed crystal. With respect to the thus prepared crystal, Laue photographs were taken in a manner similar to that in (3) of Example 1. The reflection X-ray Laue image of the $Ho_{0.5}Tb_{2.5}Al_5O_{12}$ single crystal used as the seed crystal is in agreement with that of the resulting crystal, and therefore,

it is clear that the growing orientation can be controlled as well. The material identification of the resulting crystal was performed with an X-ray diffractometer in a manner similar to that in (4) of Example 1, and no X-ray peak value other than that of the garnet phase was detected. It is clear from the above description that the resulting
5 crystal is a single phase of $\text{Ho}_{0.5}\text{Tb}_{2.5}\text{Al}_5\text{O}_{12}$ single crystal.

Example 6

As starting materials for a raw material rod, Tb_4O_7 (purity 99.9%), Al_2O_3 (purity 99.99%) and Er_2O_3 (purity 99.9%) were weighed in order to constitute $\text{ErTb}_2\text{Al}_5\text{O}_{12}$, and an $\text{ErTb}_2\text{Al}_5\text{O}_{12}$ polycrystal was prepared in a manner similar to that
10 in Example 1. The density of the resulting $\text{ErTb}_2\text{Al}_5\text{O}_{12}$ polycrystal was 80%. A crystal was prepared in a manner similar to that in Example 1 except that an $\text{ErTb}_2\text{Al}_5\text{O}_{12}$ single crystal was used as the seed crystal. With respect to the thus prepared crystal, Laue photographs were taken in a manner similar to that in (3) of Example 1. The reflection X-ray Laue image of the $\text{ErTb}_2\text{Al}_5\text{O}_{12}$ single crystal used
15 as the seed crystal is in agreement with that of the resulting crystal, and therefore, it is clear that the growing orientation can be controlled as well. The material identification of the resulting crystal was performed with an X-ray diffractometer in a manner similar to that in (4) of Example 1, and no X-ray peak value other than that of the garnet phase was detected. It is clear from the above description that the resulting
20 crystal is a single phase of $\text{ErTb}_2\text{Al}_5\text{O}_{12}$ single crystal.

Example 7

As starting materials for a raw material rod, Tb_4O_7 (purity 99.9%), Al_2O_3 (purity 99.99%) and Tm_2O_3 (purity 99.9%) were weighed in order to constitute $\text{Tm}_{1.2}\text{Tb}_{1.8}\text{Al}_5\text{O}_{12}$, and a $\text{Tm}_{1.2}\text{Tb}_{1.8}\text{Al}_5\text{O}_{12}$ polycrystal was prepared in a manner
25 similar to that in Example 1. The density of the resulting $\text{Tm}_{1.2}\text{Tb}_{1.8}\text{Al}_5\text{O}_{12}$ polycrystal was 80%. A crystal was prepared in a manner similar to that in Example 1 except that a $\text{Tm}_{1.2}\text{Tb}_{1.8}\text{Al}_5\text{O}_{12}$ single crystal was used as the seed crystal. With respect to the thus prepared crystal, Laue photographs were taken in a manner similar to that in (3) of Example 1. The reflection X-ray Laue image of the $\text{Tm}_{1.2}\text{Tb}_{1.8}\text{Al}_5\text{O}_{12}$ single crystal

used as the seed crystal is in agreement with that of the resulting crystal, and therefore, it is clear that the growing orientation can be controlled as well. The material identification of the resulting crystal was performed with an X-ray diffractometer in a manner similar to that in (4) of Example 1, and no X-ray peak value other than that of the garnet phase was detected. It is clear from the above description that the resulting crystal is a single phase of $\text{Tm}_{1.2}\text{Tb}_{1.8}\text{Al}_5\text{O}_{12}$ single crystal.

Comparative example 1

A manufacturing method similar to that in Example 1 was performed, except that an YAG laser apparatus was used as the laser apparatus 5 used for melt-joining the TAG polycrystal and the TAG single crystal in the second step in Example 1. However, it was found that the TAG polycrystal did not melt because the wavelength of the YAG laser light was $1.064\text{ }\mu\text{m}$, and therefore, the laser light was not absorbed by the TAG polycrystal having a high light-transmittance in the wide wavelength range of 0.5 to $1.6\text{ }\mu\text{m}$. Consequently, it is clear that no TAG single crystal can be produced when the YAG laser apparatus is used as a device for applying optical energy to the joint of the TAG polycrystal and the $\text{Tb}_3\text{Al}_5\text{O}_{12}$ single crystal.

Experimental example 2

TAG single crystals were prepared as starting materials for a raw material rod and a seed crystal. In addition to this, Tb_4O_7 (purity 99.9%) and Al_2O_3 (purity 99.99%) were weighed, and TAG polycrystals having densities of 55% to 90%, as shown in Table 1, were prepared. The method for manufacturing TAG polycrystals having the thus different densities was adjusted by setting the firing temperature at $1,400^\circ\text{C}$ to $1,600^\circ\text{C}$ in the first step of Example 1. The resulting TAG polycrystals were molded into the shape of a cylindrical column having a diameter of 3 mm or 1 mm. Raw material rods and seed crystals were prepared in combinations shown in Table 1, and TAG single crystals were grown in a manner similar to that in Example 1.

With respect to whether the crystal prepared as described above was a TAG single crystal, the material identification was performed with an X-ray diffractometer

which measured diffraction peaks based on the irradiation of the resulting crystal with an X-ray. The case where a single phase of TAG single crystal having a diameter of 3 mm was produced was indicated by ⊙. The case where a single phase of TAG single crystal having a diameter of 3 mm was not produced, but a single phase of TAG single crystal having a diameter of 1 mm was produced was indicated by ○. The case where a TbAlO₃ phase was deposited was indicated by ×. The case where no crystal was generated due to occurrence of crack or breaking of the melt zone was indicated by ××.

Table 1

Raw material rod Seed Crystal	50%	55%	60%	70%	80%	85%	90%	100%
50%	××	××	××	××	××	××	××	××
55%	××	⊙	⊙	⊙	⊙	⊙	⊙	⊙
60%	××	⊙	⊙	⊙	⊙	⊙	⊙	⊙
70%	××	⊙	⊙	⊙	⊙	⊙	⊙	⊙
80%	××	⊙	⊙	⊙	⊙	⊙	⊙	⊙
85%	××	⊙	⊙	⊙	⊙	⊙	⊙	⊙
90%	××	○	○	○	○	○	×	×
100%	××	○	○	○	○	○	×	×

- 10 ⊙ TAG single crystal 3 mm
 ○ TAG single crystal 1 mm
 × TAP deposition
 ×× No crystal was generated

15 As is clear from Table 1, a single phase of TAG single crystal can be produced when at least one of the raw material rod and the seed crystal is porous, one of the raw material rod and the seed crystal has a density of about 55% or more but 100% or less, and the other has a density of about 55% or more but about 85% or less.

20 In particular, it is made clear that a single phase of TAG single crystal having a diameter of 3 mm can be produced as well with respect to the crystals produced from the seed crystal having a density within the range of about 55% or more but about

85% or less and the raw material rod having a density within the range of about 55% or more but 100% or less.

On the other hand, it is made clear that TbAlO_3 is deposited in a single crystal in the case where TAG single crystal is used for both the seed crystal and the raw
5 material rod, and in the case where both the seed crystal and the raw material rod have densities exceeding about 85%. It is believed that this is because the raw material rod and the seed crystal are not porous, and therefore, an initial phase of TbAlO_3 is deposited in a single crystal by heat-melting.

In the case where both the seed crystal and the raw material rod have densities
10 of less than about 55%, the molten liquid excessively penetrates into the holes, and thereby, the single crystal becomes too slender, so that the melt zone is broken or cannot be stably held.